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Griessen, R.

published in
Physical Review B. Condensed Matter
1987

document version
Publisher's PDF, also known as Version of record

Pressure dependence of high-T_c superconductors

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(Received 10 July 1987)

The pressure dependence of the transition temperature of high-T_c superconductors is considered within the framework of the standard Bardeen-Cooper-Schrieffer (BCS) electron-phonon theory, the bidimensional BCS theory, the resonating-valence-bond theories, and various bipolaronic superconductivity models.

I. INTRODUCTION

High-T_c superconductivity has been reported to occur in Ba-La-Cu-O, La-Sr-Cu-O, Y-Ba-Cu-O, and other compounds involving rare earths.[1,2] Already in the early stage of research on these perovskitelike compounds Chu *et al.*[3] demonstrated that in Ba-La-Cu-O the critical temperature could be increased drastically under pressure. The value $dT_c/dp = 0.64$ K (kbar)$^{-1}$ was the highest pressure derivative ever observed in a superconductor. In sharp contrast to Ba-La-Cu-O, the Y-Ba-Cu-O system exhibits only a very weak increase of the onset temperature T_{co} with increasing pressure. In the low-pressure regime up to 19 kbar Hor *et al.*[4] found $dT_{co}/dp = 0.05$ K (kbar)$^{-1}$, and recently Driessen *et al.*[5] reported a value $dT_{co}/dp = 0.043$ K (kbar)$^{-1}$ obtained from high-pressure experiments in a diamond-anvil cell up to 170 kbar.

Until now various mechanisms have been proposed to explain the remarkable behavior of high-T_c superconductors under high pressure.

(i) Chu *et al.*[3] remarked that the large dT_c/dp of La-Ba-Cu-O is consistent with the occurrence of interfacial superconductivity between a superconducting metal and a semiconductor. Pressure in that case acts as a continuous parameter with which it is possible to optimize the coupling between both constituents, the Fermi energy of the metal and the band gap of the semiconductor. Within this interpretation it is not clear why Y-Ba-Cu-O should be so different from La-Ba-Cu-O.

(ii) For $La_{2-x}(Ba,Sr)_xCuO_4$ Weber[6] calculated the Eliashberg $\alpha^2F(\omega)$ function by means of the nonorthogonal tight-binding theory of lattice dynamics. He showed that when lanthanum is partially substituted by a divalent metal (Ba or Sr) the static Peierls distortion discussed by Mattheiss[7] for La_2CuO_4 disappears and that giant Kohn anomalies exist near the Brillouin-zone boundary for oxygen breathing modes. The stability of the Peierls distortion depends on the force constant f_2 of the planar Cu—O bond. For a superconductor with, for example, $x = 0.2$ the results of Fig. 3 in Ref. 6 imply that $d\ln T_c/d\ln f_2 = -4.4$. Under pressure f_2 is expected to increase. Unfortunately, the Grüneisen parameter corresponding to modes determined by f_2 have not been determined yet. For an estimate we use the high-pressure results of Sugiura and Yamadaya[8] on $BaBiO_3$. They found from Raman scattering experiments at pressures up to 180 kbar that the stretching mode frequency ω of the BiO_6 octahedra varies linearly with volume, so that $d\ln\omega/d\ln V = -1.4$. For f_2 in Ba-La-Cu-O one thus expects similarly $d\ln f_2/d\ln V \cong -2.8$ as $f_2 \propto \omega^2$. With a compressibility of 6×10^{-7} bar^{-1} we find finally that $d\ln T_c/dp \cong -7.4\times10^{-3}$ (kbar)$^{-1}$ which, for $T_c = 32$ K, leads to $dT_c/dp \cong -0.24$ K (kbar)$^{-1}$. This is too small in magnitude, and furthermore, it has the *wrong* sign. Within the normal band-structure electron-phonon interaction formalism it is thus not possible to understand the large increase of T_c with pressure.

Weber suggested, however, that dT_c/dp might be large for *inhomogeneous* samples, e.g., samples in which spinodal decomposition waves lead to spatial fluctuations in x. An increase in f_2 under pressure pushes the Peierls instability to smaller values of x where higher electron-phonon enhancement factors λ are possible without destroying the lattice stability. As follows from the lattice stability line in Fig. 3 of Ref. 6, T_c increases *on* this line approximately as $d\ln T_c/d\ln f_2 = 1.5$. Using the same estimates as above one then obtains $dT_c/dp \simeq 0.08$ K (kbar)$^{-1}$. Thus even if one assumes that under pressure regions of the sample with Ba (or Sr) concentrations smaller than the nominal concentration become superconducting because of an increase in f_2 with pressure, one still obtains values for dT_c/dp which are almost one order of magnitude smaller than found experimentally. Furthermore, as pointed out in Ref. 5, the spatial concentration fluctuations required to explain a large and positive dT_c/dp would lead to a considerable smearing out of the transition and, in particular, to a lowering of the midpoint transition with increasing pressure, in sharp contrast to the experimental data.[3]

(iii) Hor *et al.*[4] suggested that the weak pressure dependence of T_c for Y-Ba-Cu-O might be due to the "chemical" pressure already present due to the replacement of La by Y. To check the validity of this argument we use the recent structure studies of Capponi *et al.*,[9] and Beno *et al.*[10] for $YBa_2Cu_3O_7$ and Jorgensen *et al.*[11] for $La_{1.85}Ba_{0.15}CuO_4$. In $YBa_2Cu_3O_7$ the four nearest oxygen neighbors are at an average distance of 1.92 Å from a copper atom. In $La_{1.85}Ba_{0.15}CuO_4$ there are four oxygen atoms at a distance of 1.90 Å. On the basis of this argument one would therefore conclude that the Cu—O bonds are rather insensitive to the "chemical" pressure mentioned by Hor *et al.*[4]

On the other hand, if one simply considers that the average volume per atom, $\Omega = 13.3$ Å^3 for $YBa_2Cu_3O_7$, is significantly smaller than $\Omega = 27.2$ Å^3 for $La_{1.85}Ba_{0.15}CuO_4$ or $\Omega = 26.9$ Å^3 for $La_{1.85}Sr_{0.15}CuO_4$, $YBa_2Cu_3O_7$ may then be considered as a "compressed" Ba-La-Cu-O,

TABLE I. Pressure and volume dependence of the onset temperature T_{co}, the midpoint temperature T_c, and the temperature T_{cf} at which the transition is completed. For the conversion of pressure derivatives to volume derivatives we used $B = 1600$ kbar for the bulk modulus of La-Ba-Cu-O and La-Sr-Cu-O and $B = 1700$ kbar for Y-Ba-Cu-O. The pressure range for each experiment is indicated in the column p. The symbols in the last column are used in Fig. 1.

Sample	T_{co} (K)	T_{co} (K)	T_{cf} (K)	p (kbar)	dT_{ci}/dp (K/kbar)	$d\ln T_{ci}/dp$ (10^{-2} kbar^{-1})	$\frac{d\ln T_{ci}}{d\ln V}$	Symbol, Ref.
$La_{1.25}Sr_{0.15}CuO_{4-y}$		36		≤ 10	0.28	7.78	−12.4	△, 15
$La_{1.8}Sr_{0.2}CuO_{4-y}$	37			≤ 20	0.12	0.32	−5.2	▲, 16
	37				0.32	0.87	−13.9	▲, 16
La_2CuO_4	≈ 40			≤ 10	1.05	2.63	−42	◑, 17
$La_{0.8}Ba_{0.2}CuO_{3-y}$	32			≤ 17	0.64	2.00	−32.0	●, 3
$La_{1.85}Ba_{0.15}CuO_{4-y}$	35.2			≤ 19	0.32	0.90	−14.5	◐, 18
		30.4			0.17	0.56	−8.9	◐, 18
			26.0		0.13	0.50	−8.0	◐, 18
$Y_{0.325}Ba_{0.675}CuO_{2.3}$	92			≤ 10	0.17	0.19	−3.1	□, 19
			84		0.40	0.48	−8.1	□, 19
$Y_{0.35}Ba_{0.65}CuO_{2.3}$	93			≤ 10	0.10	0.11	−1.8	◪, 19
			79.5		0.20	0.25	−4.3	◪, 19
$Y_{0.425}Ba_{0.575}CuO_{2.3}$	93.5			≤ 10	0.09	0.01	−1.6	◪, 19
			83.6		0.28	0.34	−5.7	◪, 19
$Y_{0.4}Ba_{0.6}CuO_{3-y}$		89.7		≤ 9.5	−0.25	−0.28	4.7	▽, 20
$YBa_2Cu_3O_7$	90			≤ 18	~0	~0	~0	▼, 21
		87			~0	~0	~0	▼, 21
			85		~ −0.30	~ −0.35	~6.0	▼, 21
$(Y_{0.6}Ba_{0.4})_2CuO_{4-\delta}$	91.5			≤ 19	0.114	0.13	−2.1	▼, 4
			88.5		−0.079	0.09	1.5	▼, 4
$YBa_2Cu_3O_7$	91			≤ 170	0.043	0.047	−0.80	⊛, 5
			88		−0.070	0.080	1.35	⊛, 5
$Y_{1.2}Ba_{1.8}Cu_3O_{6.6}$	92			≤ 120	0.045	0.049	−0.83	✳, 22
			87		−0.060	0.069	1.17	✳, 22

although the value of such reasoning is highly questionable.

From the foregoing it is quite clear that a coherent description of the pressure dependence of T_c in metal oxide is still lacking. In this work we *assume* that the observed properties of high-T_c superconductors are *bulk* properties and show that the normal BCS approach cannot account for the various dT_c/dp values measured so far for superconducting metal oxides. To simplify the comparison of theory and experiment it is useful first to convert the pressure derivatives dT_c/dp into relative volume derivatives $d\ln T_c/d\ln V$. From the measurements of Salomons *et al.* [12] we estimate that the bulk modulus of $YBa_2Cu_3O_{7.1}$ is $B \cong 1700$ kbar. From the pressure data of Driessen *et al.* [5] and Hor *et al.* [4] it then follows that

$$\frac{d\ln T_c}{d\ln V} \cong -0.8 \ , \tag{1}$$

and from the data of Chu *et al.* for $YBa_2Cu_3O_{7.1}$ that

$$\frac{d\ln T_c}{d\ln V} \simeq -32 \tag{2}$$

if one uses the same bulk modulus value for Ba-La-Cu-O as that measured by Takahashi *et al.* [13] and Terada *et al.* [14] ($B \simeq 1600$ kbar).

Very recently Allgeier *et al.* [15] reported that for $La_{1.85}Sr_{0.15}CuO_4$ T_c also increases rapidly with pressure ($p < 10$

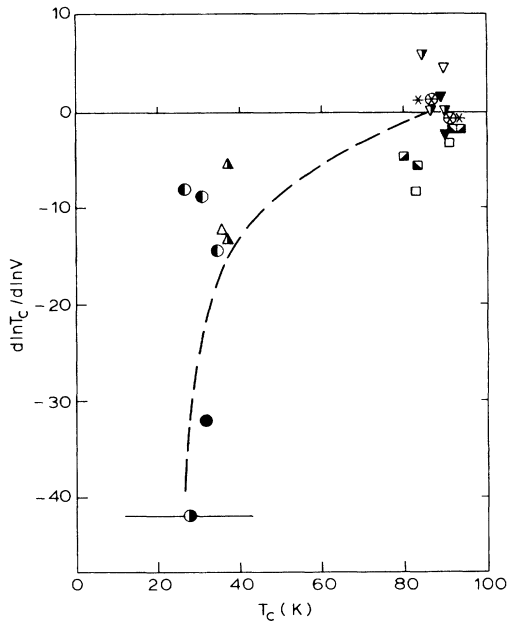

FIG. 1. Relative volume dependence of T_c as a function of T_c. The symbols are defined in Table I. The error bar for La_2CuO_4 reflects the uncertainty in defining a midpoint transition temperature for this oxide (Ref. 17). The large scatter of points for Y-Ba-Cu-O ($T_c > 80$ K) is probably due to the use of polyphased samples in the earlier investigations.

kbar) at the rate of $dT_c/dp = 0.28$ K (kbar)$^{-1}$. With $T_c = 36$ K and $B \cong 1600$ kbar we then obtain

$$\frac{d\ln T_c}{d\ln V} = -12.4 \ . \tag{3}$$

More experimental values are given in Table. I. Quite impressive is the good agreement between the measurements of Okai, Takahashi, and Ohta[22] and Driessen *et al.*[5] on Y-Ba-Cu-O in the high-pressure regime. The data in Table I also exhibit a general trend for $d\ln T_{ci}/d\ln V$. For the superconductors with the highest T_{ci} the volume dependence of the transition temperature is especially weak. This is clearly shown in Fig. 1.

II. BCS THEORY WITH ELECTRON-PHONON INTERACTION

For the discussion of the volume dependence of T_c within the standard BCS model we start from the expression of Allen and Dynes[23]

$$T_c = \frac{\Theta_{\log} f_1 f_2}{1.2} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right] , \tag{4}$$

with

$$f_1 = \{1 + [\lambda/(2.46+9.35\mu^*)]^{3/2}\}^{1/3} , \tag{5}$$

$$f_2 = 1 + \frac{(\bar{\omega}_2/\omega_{\log} - 1)\lambda^2}{\lambda^2 + (1.82+11.5\mu^*)^2 \bar{\omega}_2^2/\omega_{\log}^2} , \tag{6}$$

with

$$\omega_{\log} \equiv \exp\left[\frac{2}{\lambda} \int_o^\infty \frac{\ln\omega}{\omega} \alpha^2 F(\omega) d\omega \right] , \tag{7}$$

and

$$\bar{\omega}_2 = \left[\int_0^\infty \omega \alpha^2 F(\omega) d\omega \Big/ \left[\int \frac{\alpha^2 F(\omega)}{\omega} d\omega \right] \right]^{1/2} . \tag{8}$$

μ^* is the conventional Coulomb pseudopotential, λ the electron-phonon enhancement parameter, $\Theta_{\log} \equiv \hbar\omega_{\log}/k_B$, and $\alpha^2 F(\omega)$ the Eliashberg function. λ and $\alpha^2 F(\omega)$ are related to each other by

$$\lambda = 2\int_0^\infty \frac{\alpha^2 F(\omega) d\omega}{\omega} . \tag{9}$$

The Eliashberg function has not been calculated for the high-T_c superconductors (except La_2CuO_4) until now. From numerical examples we conclude, however, that $\bar{\omega}_2 \simeq \omega_{\log}$ and that $f_2 \simeq 1$. For simplicity we set $f_2 = 1$. We also assume that μ^* is volume independent. The critical temperature is then given by an expression of the form

$$T_c = \Theta_{\log} f(\lambda, \mu^*) \tag{10}$$

and its volume derivation can be written

$$\frac{d\ln T_c}{d\ln V} = -\gamma_{\log} + g(\lambda,\mu^*) \frac{d\ln\lambda}{d\ln V} \tag{11}$$

with

$$g(\lambda,\mu^*) = \frac{1.04(1+0.38\mu^*)\lambda}{[\lambda - \mu^*(1+0.62\lambda)]^2} + \frac{\lambda^{3/2}}{2[\lambda^{3/2} + (2.46+9.35\mu^*)^{3/2}]} , \tag{12}$$

and

$$\gamma_{\log} \equiv -d\ln\Theta_{\log}/d\ln V \ .$$

If for μ^* we choose the canonical value 0.13 the function $g(\lambda)$ is well approximated by the following simple expression

$$g(\lambda) \simeq 0.4 + (1/\lambda) \tag{13}$$

in the range $1.5 \leq \lambda \leq 10$ relevant to high-T_c superconductors. From Eqs. (11) and (13) then directly follows that a volume derivative as large as that observed in Ba-La-Cu-O [(Eq. (2)] is not possible within the standard electron-phonon BCS theory unless unrealistically large Grüneisen parameters or strongly volume-dependent electron-phonon enhancement parameters are assumed. To be more specific we express λ in terms of the electronic electron-phonon interaction parameter η and the phononic part $M\langle\omega^2\rangle$. We have then

$$\frac{d\ln\lambda}{d\ln V} = \frac{d\ln\eta}{d\ln V} + 2\langle\gamma\rangle \tag{14}$$

with

$$\langle\gamma\rangle \equiv -\frac{d\ln(\langle\omega^2\rangle^{1/2})}{d\ln V} \tag{15}$$

as $\lambda = \eta/M\langle\omega^2\rangle$. As $\langle\gamma\rangle \simeq \gamma_{\log}$ it follows from Eqs. (11), (13), and (14) that for large λ

$$\frac{d\ln T_c}{d\ln V} \simeq 0.5 \frac{d\ln\eta}{d\ln V} \ . \tag{16}$$

For many superconductors[24] $d\ln\eta/d\ln V \simeq -2$, so that $d\ln T_c/d\ln V \simeq -1$, which is much smaller than the values given in Eqs. (1)–(3) or Table I.

III. BIDIMENSIONAL BCS MODEL

Recently Labbé and Bok[25] presented a model for the superconductivity of a nearly half-filled two-dimensional lattice. Because of the bidimensional character the electronic density of states $n(E)$ has a logarithmic divergence at the energy E_s corresponding to an exactly half-filled band. Near E_s,

$$n(E) = \frac{N}{\pi^2 D} \ln\left[\frac{D}{|E - E_s|} \right] , \tag{17}$$

where D is the "width" of the singularity given by

$$D = \frac{\gamma^2}{[(E_d - E_p)^2 + 16\gamma^2]^{1/2}} , \tag{18}$$

where γ is the transfer integral between $d_{x^2-y^2}$ and p_x or-

bitals and N is the number of unit cells. In Eq. (18) $E_d - E_p$ is the difference between the energy of copper $3d$ and oxygen $2p$ states. By assuming that E_F coincides with E_s, Labbé and Bok obtained the following expression for T_c, in the weak-coupling limit

$$k_B T_c = 1.13 \hbar D \exp[(-1/\sqrt{\lambda})] \ . \tag{19}$$

This relation shows explicitly that the cutoff energy of interest is determined by the width of the logarithmic van Hove singularity and not by the phonon frequency. For the volume dependence of T_c one finds by simple differentiation of Eq. (19) that

$$\frac{d\ln T_c}{d\ln V} = \frac{d\ln D}{d\ln V} + \frac{1}{2\sqrt{\lambda}} \frac{d\ln\lambda}{d\ln V} \ . \tag{20}$$

From Eq. (18) it follows that $d\ln D/d\ln V \simeq d\ln t_b/d\ln V \approx -1$ if the volume dependence of $E_d - E_p$ is neglected. To calculate the contribution of the second term in Eq. (20) we need to evaluate λ. As the width W_b of the band is $W_b = 8t_b$, we estimate from the band-structure calculations of Mattheiss,[7] Oguchi,[26] and Yu, Freeman, and Xu[27] that $\gamma \simeq 1.4$ eV, $D \simeq 0.3$ eV, and, consequently, $\sqrt{\lambda} \cong 0.27$ corresponds to $T_c = 95$ and $\sqrt{\lambda} \simeq 0.21$ to $T_c = 32$ K (Ba-La-Cu-0).

In Fig. 2 we indicate how $d\ln T_c/d\ln V$ varies with T_c for two different cases: (i) with $d\ln D/d\ln V = -1$, $d\ln\lambda/d\ln V = -2$, and $D = 0.3$ eV; and (ii) with $d\ln D/d\ln V = 4$, $d\ln\lambda/d\ln V = -3$, and $D = 0.3$ eV. This second case is chosen to show that the trend in Fig. 1 may be qualitatively reproduced by means of a two-dimensional (2D) BCS theory. The assumed positive value of $d\ln D/d\ln V$ implies, however, that $E_d - E_p$ is strongly volume dependent. Band-structure calculations at various volumes would be required to clarify this assumption.

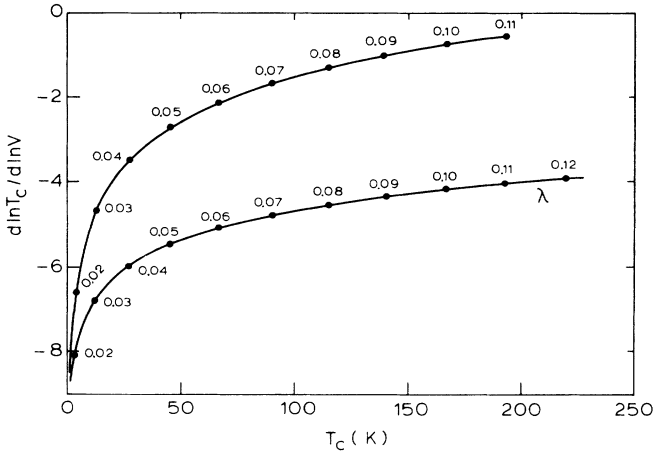

FIG. 2. Relative volume dependence of T_c as a function of T_c according to the Labbé and Bok model. T_c is calculated by means of Eq. (19) with $D = 0.3$ eV for the width of the logarithmic singularity in the density of states at E_F. The volume derivatives $d\ln T_c/d\ln V$ are obtained from Eq. (20) with $d\ln\lambda/d\ln V = -2$ and $d\ln D/d\ln V = -1$ (——) and $d\ln\lambda/d\ln V = -3$ and $d\ln D/d\ln V = 4$ (---). The values indicated correspond to λ.

To conclude this subsection on standard BCS theory (with electron-phonon coupling) it is worth mentioning that from the magnetic-susceptibility measurements of Allgeier *et al.*[15] it follows that $|d\ln N(E_F)/d\ln V| \gtrsim 3$ in $La_{1.85}Sr_{0.15}CuO_4$. The large $d\ln\lambda/d\ln V$ which would be required within the 2D or 3D BCS theory to explain the high $d\ln T_c/d\ln V$ would therefore imply very large volume dependence of the effective attractive interaction $V_{\text{el-ph}}$ as $\lambda = N(E_F)V_{\text{el-ph}}$.

IV. RESONATING-VALENCE BONDS

From structural information on La_2CuO_4 Anderson[28] concluded that the Cu^{2+} ions were in an $S = \frac{1}{2}$ singlet state, strongly hybridized with the p levels of the nearest oxygen atoms. On the basis of an earlier article[29] he proposed that, certainly for the two-dimensional triangular antiferromagnet with $S = \frac{1}{2}$, and probably for other lattices, the ground state might be the analog of the precise singlet in Bethe's solution of the one-dimensional antiferromagnetic chain.[30] Both for the linear chain and the triangular lattice he showed that a state consisting only of nearest-neighbor singlet pairs is more realistic than the regular spin-up, spin-down arrangement of the Néel state. Further lowering of the ground-state energy is obtained by allowing the singlet pairs to tunnel through the lattice. These qualitative statements are supported by the numerical simulations of Hirsch[31] for the 2D square-lattice Hubbard model with various band fillings.

For the resonating-valence-bond models in the strong-coupling limit ($t_b^2 < U$) Anderson[28] proposes that $T_c \lesssim t_b^2/U$, where t_b is the single-electron hopping integral for the noninteracting system ($U = 0$). U is the local electron-electron repulsion for electrons of opposite spins in the same atomic orbital. For a two-dimensional square lattice the width W_b of the electronic band is $W_b = 8t_b$. For the volume dependence of T_c it then follows that

$$\frac{d\ln T_c}{d\ln V} = 2\frac{d\ln W_b}{d\ln V} - \frac{d\ln U}{d\ln V} \ . \tag{21}$$

For pure d bands,[32] $d\ln W_b/d\ln V = -\frac{5}{3}$ and for free electrons $d\ln W_b/d\ln V = -\frac{2}{3}$. For most pure metals the *electronic* Grüneisen parameter[33] $\gamma_e \equiv [d\ln N(E_F)]/d\ln V \cong -d\ln W_b/d\ln V$ varies between 0.2 and 2. For the present discussion we take $d\ln W_b/d\ln V \simeq -1$. U being essentially an intrasite parameter, we expect that $d\ln U/d\ln V \simeq 0$ so that, typically, $d\ln T_c/d\ln V \simeq -2$.

As for the standard BCS theory with (strong) electron-phonon interaction, we see that the resonating-valence-bond model (in the form presented above) is not able to reproduce the large $d\ln T_c/d\ln V \cong -32$ observed in Ba-La-Cu-O.

In a recent paper Fukuyama and Yosida[34] explored some implications of the mechanism proposed by Anderson.[28] Starting from the nondegenerate Hubbard model

$$H = \sum t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} + U \sum n_{i\uparrow} n_{i\downarrow} \tag{22}$$

with the transfer integral t_b between nearest neighbors,

they find in the limit $U \gg t_b$ that T_c is given by

$$k_B T_c = 1.13 \hbar \omega_0 \exp\left[-\frac{1}{\lambda(n)}\right] \tag{23}$$

with

$$\lambda(n) = \frac{8}{\pi}\frac{t_b}{U}\Phi(n) , \tag{24}$$

where $\Phi(n)$ depends only on the electron density per site, $n=1$ corresponding to the case of a half-filled band. The cutoff energy $\hbar\omega_0$ is of the order of t_b. From Eqs. (23) and (24) it then follows that

$$\frac{d\ln T_c}{d\ln V} \cong \frac{d\ln t_b}{d\ln V}\left[1+\frac{1}{\lambda(n)}\right] \tag{25}$$

if, as before, $d\ln U/d\ln V$ is taken to be zero. With $\hbar\omega_0 = 0.2 t_b = 0.08$ eV (Refs. 7, 26, and 27) we find from Eq. (23) that $\lambda \cong 0.4$ corresponds to $T_c = 95$ K and $\lambda \cong 0.3$ to $T_c = 32$ K for a nearly half-filled band ($n=0.9$). In this version of the resonance-valence-bond model we thus see that moderately high values for $d\ln T_c/d\ln V$ are possible $(-3, \ldots, -8)$. The values of λ mentioned above (0.3, 0.4) imply, however, that $t_b \simeq U$. The use of the effective Hubbard Hamiltonian derived by Hirsch[31] for the case $t_b \ll U$ is therefore questionable.

Using the approach he proposed in the context of heavy-electron systems, Cyrot[35] obtained the following expression for T_c:

$$T_c \simeq t_b \delta \exp(-U\delta/t_b) , \tag{26}$$

where δ is the fractional doping which creates some Cu^{3+} ions instead of Cu^{2+}. This expression for T_c has a maximum for $\delta = t_b/U$. For this value $T_c = t_b^2/U$ as predicted by Anderson for his resonating-valence-band model.

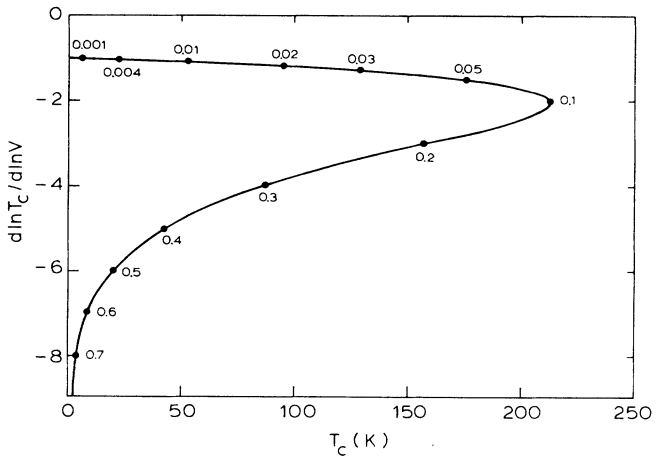

FIG. 3. Relative volume dependence of T_c as a function of T_c according to the model of Cyrot. T_c is calculated by means of Eq. (26) with $t_b = 0.5$ eV and $U=5$ eV. The corresponding $d\ln T_c/d\ln V$ are obtained from Eq. (27) with $d\ln t_b/d\ln V = -1$. The values indicated correspond to the fractional doping δ.

From Eq. (26) it follows that

$$\frac{d\ln T_c}{d\ln V} = \frac{d\ln t_b}{d\ln V}\left[1+\frac{U\delta}{t_b}\right] . \tag{27}$$

In Fig. 3 we represent $d\ln T_c/d\ln V$ as a function of T_c for the case $t_b = 0.5$ eV, $U=5$ eV, and $d\ln t_b/d\ln V = -1$. For fractional doping $\delta > 0.1$, $d\ln T_c/d\ln V$ becomes more and more negative while T_c decreases. This behavior is in qualitative agreement with the experimental data shown in Fig. 1.

V. MANY-POLARONIC SUPERCONDUCTIVITY

Before discussing bi- or many-polaronic superconductivity it is useful to determine which values of the electron-phonon enhancement parameter λ are required to reproduce $T_c \geq 35$ K within the framework of the standard strong-coupling BCS theory.[23]

We consider first Ba-La-Cu-O for which Weber[6] has made quantitative calculations of λ. From Fig. 3 in Ref. 6 it follows that $T_c = 35$ K for $\lambda = 2.5$ and a planar Cu—O band-stretching force constant $f_2 = 11$ eV/Å^2. The corresponding $\Theta_{\log}$ determined from Eq. (3) by setting $T_c = 35$ K, $\lambda = 2.5$, and $\mu^* = 0.13$ is $\Theta_{\log} = 194$ K. To obtain $T_c = 95$ K with the same $\Theta_{\log}$ we would need $\lambda = 13.5$. Even with a significant higher $\Theta_{\log}$, say $\Theta_{\log} = 400$ K, we still need $\lambda = 3.75$. As discussed by Cyrot,[35] Chakraverty,[36] Anderson and Cohen,[37], Rice and Sneddon,[38] Alexandrov and co-workers,[39,40] and Nasu[41] in the limit of large electron-phonon coupling bipolaron formation may occur. The condition for bipolaron formation is essentially the same as that for strong coupling in the standard BCS theory, $\lambda > 1$, i.e.,

$$\frac{2zg^2\hbar\omega}{W_b} > 1 , \tag{28}$$

where W_b is the width of the *bare* (i.e., unrenormalized) electron band, z the number of nearest neighbors in the lattice under investigation, ω a characteristic phonon frequency, and g a dimensionless parameter characterizing the strength of the electron-phonon interaction defined as

$$g^2 \equiv \sum_{\mathbf{q}} \frac{|U(\mathbf{q})|^2[1-\cos(\mathbf{q}(\mathbf{R}_m - \mathbf{R}_{m'})]}{\hbar^2\omega_{\mathbf{q}}^2} , \tag{29}$$

where $U(\mathbf{q})$ is the Fourier transform of the electron-lattice interaction and $\mathbf{R}_m$ is the position of the mth sites. For a square density of states $W_b = 1/N(E_F)$, where $N(E_F)$ is the *bare* electronic density of states at the Fermi energy and Eq. (28) can be written in the usual form:

$$\bar{V}N(E_F) > 1 , \tag{30}$$

with $\bar{V} = 2zg^2\hbar\omega$ as the phonon-mediated attractive interaction. Starting from the usual Fröhlich interaction, Alexandrov, Ranninger, and Robaskiewicz[40] derived the following equation for the superconducting T_c:

$$\frac{1}{2n_b - 1} = \frac{1}{N}\sum_{\mathbf{k}} \coth\left[\frac{(2n_b-1)}{2k_B T_c}(t-t_{\mathbf{k}})\right] , \tag{31}$$

where n_b is the concentration of bipolarons, N the number

of sites in the lattice, and

$$t=\frac{2zt_b^2}{\Delta}\exp(-2g^2) , \tag{32}$$

$$t_{\mathbf{k}}=\frac{t}{z}\sum_{\mathbf{R}_m}e^{i\mathbf{k}\cdot\mathbf{R}_m} , \tag{33}$$

$$\Delta\simeq 2g^2\hbar\omega - V_0 , \tag{34}$$

where t_b is the *bare* electron hopping integral ($W_b=8t_b$ for a square lattice) and V_0 the Coulomb repulsion. Equation (32) pertains to the case where $k_BT_c<\Delta<\hbar\omega$. (For the case $\hbar\omega\ll\Delta$, see Ref. 5.)

Without solving Eq. (31) we obtain, by differentiating with respect to volume, both sides of Eq. (31),

$$\frac{d\ln T_c}{d\ln V}=\frac{d\ln t}{d\ln V}=2\frac{d\ln t_b}{d\ln V}-\frac{d\ln\Delta}{d\ln V}-2g^2\frac{d\ln g^2}{d\ln V} \tag{35}$$

if one neglects the volume dependence of V_0. Equation (35) leads to

$$\frac{d\ln T_c}{d\ln V}=2\frac{d\ln W_b}{d\ln V}+\frac{\gamma}{1-\nu_0}-\left[2g^2+\frac{1}{1-\nu_0}\right]\frac{d\ln g^2}{d\ln V} , \tag{36}$$

where $\gamma\equiv -d\ln\omega/d\ln V$ and $\nu_0\equiv V_0/(2\hbar\omega g^2)$ is the ratio of the Coulomb repulsion to the polaronic level shift $2\hbar\omega g^2$. As bipolaron formation is required for the existence of superconductivity we have necessarily $\nu_0<1$. One interesting feature of Eq. (36) is that it may lead to large volume derivatives for T_c. To illustrate this point we note that the set of parameters $z=4$, $g^2=4$, $\hbar\omega=74$ meV (corresponding to a Cu—O stretch bond[6] of 600 cm^{-1}), $W_b=2.4$ eV, and $V_0=0.54$ eV satisfy Eq. (28) and the condition $k_BT_c<\Delta<\hbar\omega$ as $\Delta=52$ meV. We have $T_c\cong 0.3t=28$ K (see Fig. 4 in Ref. 40) and

$$\frac{d\ln T_c}{d\ln V}\cong 2\frac{d\ln W_b}{d\ln V}+11\gamma-19\frac{d\ln g^2}{d\ln V} . \tag{37}$$

With $d\ln g^2/d\ln V=2$, $\gamma=1$, and $d\ln W_b/d\ln V=-1$ one then obtains, for example, $d\ln T_c/d\ln V=-31$. For this example, the bipolaron binding energy Δ is larger than the renormalized polaronic half-band width

$$W_p=\frac{W_b}{2}\exp(-g^2) , \tag{38}$$

which is equal to 22 meV. In this regime of strong polaron-polaron coupling, local small bipolarons occur. As the value assumed for the Coulomb repulsion is relatively small the bipolarons are probably involving polarons on adjacent atoms rather than polarons located on the same atom.[40]

Micnas, Ranninger, and Robaskiewicz[42] proposed recently an extension of their bipolaronic theory of superconductivity. In order to investigate the formation of electron pairs in the regime of moderately strong electron-lattice coupling they consider a system consisting of a mixture of wide- and narrow-band electrons. The narrow-band electrons are able to induce a strong polarization of the surrounding ligands, which in turn leads to the formation of local bipolarons. The hybridization of these narrow-band electrons with the wide-band electrons provides a new mechanism for superconductivity in which the local pair formation leads to quasibosons and the itinerant electrons play the role of Cooper pairs. Micnas *et al.*[42] expect that the maximum value for T_c is obtained when the concentration of both types of electrons is roughly equal. Then

$$k_BT_c\sim\hbar\frac{I^2}{W_w} , \tag{39}$$

where I is the hybridization coupling between the two bands and W_w is the width of the wide band. As $I\sim\exp(-2g^2)$ we find for the volume dependence of T_c

$$\frac{d\ln T_c}{d\ln V}\cong -4g^2\frac{d\ln g^2}{d\ln V}-\frac{d\ln W_w}{d\ln V} . \tag{40}$$

In the intermediate electron-lattice coupling regime one expects $g^2\approx 2$, so that with $d\ln g^2/d\ln V=2$ and $d\ln W_w/d\ln V=-1$ again relatively large values of $d\ln T_c/d\ln V$ are possible ($d\ln T_c/d\ln V=-15$).

VI. CONCLUSIONS

The dT_c/dp data available until now for high-T_c superconductors indicate that $d\ln T_c/d\ln V$ assumes very large negative values for the "low" high-T_c metal oxides La_2CuO_4, La-Sr-Cu-O, and La-Ba-Cu-O, while it is essentially zero for Y-Ba-Cu-O. Among the several theoretical models considered in this work only (i) the two-dimensional BCS model of Labbé and Bok,[25] (ii) the resonating-valence-bond-like models (as treated by Fukuyama and Yosida[34] and Cryot[35]), and (iii) the bipolaronic model of Alexandrov, Ranninger, and Robaszkiewicz[40] are able to reproduce large values for $d\ln T_c/d\ln V$ without having to assume unrealistically large values for $d\ln\lambda/d\ln V$ or $d\ln t_b/d\ln V$ for the electron-phonon enhancement parameter λ or the bare overlap integral t_b.

In the light of the recent measurements of the absence of isotope effect[43,44] in $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$ it is worthwhile to mention that the 2D BCS model may be weakly dependent on the isotope mass while any bipolaronic model is necessarily strongly isotope dependent. On the basis of the present analysis of dT_c/dp *and* of the absence of isotope effect one would thus favor the approach of Fukuyama and Yoshida or that of Cyrot. However, both more experimental and theoretical work is clearly needed for an unambiguous identification of the mechanism responsible for high-T_c superconductivity. We hope that the present work will stimulate theorists to discuss explicitly in the future the implications of their models for the volume dependence of T_c.

ACKNOWLEDGMENTS

I am grateful to J. Ranninger and T. M. Rice for interesting discussion and to A. Driessen and H. Hemmes for their valuable contribution to the investigation of the pressure dependence of T_c.

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